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Report Title

Final Report: Acquisition of an X-Ray Scattering System with Solid-Gas Reactor Chamber and Ultrafast Detection Capabilities for Research and Instruction in Science and Engineering

ABSTRACT

This project was aimed at the acquisition of an x-ray scattering system for research and student instruction. We purchased a Panalytical Empyrean with unique sample-environment-control capabilities that enable studies of functional materials under their actual operating conditions. The system has been installed, commissioned and is fully functional. Moreover, the system became the centerpiece of a new x-ray core facility that now includes three diffractometers (two powder and one single crystal). Following the DoD-HBCU sponsorship of this project, UTEP provided internal funding for the single crystal system – a Bruker D8 Quest (December 2014), for the renovation of two rooms to house the facility (February 2015), and for the hiring of a postdoctoral researcher to oversee its day-to-day operations (January 2015). The internal funding amount was \$390,000. The facility is now operational and has begun serving its main two objectives: 1) research aimed at investigating the atomic level structures and dynamics that govern the enhanced proton conductivity in compounds that can function as fuel cell electrolytes at intermediate temperatures (e.g. doped Sn-pyrophosphates and phosphate-solid-acid/silica composites), and 2) instruction of student-faculty teams in acquiring skills and experiences necessary to actively participate in a UTEP – National Laboratory collaborative program.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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Number of Papers published in peer-reviewed journals:

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| | Graduate Students |

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| Mustafa Golam | 0.00 | |
| Heber Martinez | 0.00 | |
| Israel Martinez | 0.00 | |
| Joshua Morris | 0.00 | |
| Alex Price | 0.00 | |
| Andres Encerrado | 0.00 | |
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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

- Synchrotron x-ray diffraction experiments on InxSn1-xP2O7 carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure x-ray diffraction on CsH2PO4 and RbH2PO4 carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure neutron diffraction work on CsH2PO4 and RbH2PO4 carried out at the Manuel Lujan Neutron Scattering Center (Los Alamos National Laboratory)
- Neutron vibrational spectroscopy carried out on CsH2PO4 at the Manuel Lujan Neutron Scattering Center (Los Alamos National Laboratory)
- Met with Dr. Andrew Dattelbaum, MPA-11 Group Leader at Los Alamos National Laboratory, discussed the possibility of joint research projects involving UTEP students and faculty and MPA-11 researchers. Dr. Dattelbaum visited UTEP, met with the Dean of the College of Science. We wrote a grant proposal to initiate a UTEP LANL partnership to the Nuclear Regulatory Commission in 2014 proposal was recommended funding, but funding decision was postponed due to limited budget.
- Communicated with Dr. Chi-Chang Kao, director of SLAC National Laboratory. PI will visit SLAC in the Spring of 2015 to discuss potential collaborations with scientists at the SSRL synchrotron and write joint grant proposal aimed at funding research and student instruction partnership.

FINAL REPORT - Grant # 64705CHREP

(Reporting Period: February 2014 – January 2015)

Acquisition of an X-ray Scattering System for Research and Instruction in Science and Engineering

PI Name: Cristian E. Botez

Department: Physics

The University of Texas at El Paso, El Paso, TX 79968

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1 STATEMENT OF THE PROBLEM

1.1. Objective

The project consists of the acquisition, installation, commissioning and operation of a Panalytical Empyrean powder X-ray diffractometer equipped with an Anton Paar XRK 900 solid-gas reaction chamber and an ultrafast PIXcell^{3D} detector. The instrument enables studies of functional materials under their actual operating conditions and is used by faculty members in Physics, as well as in other departments in the Colleges of Science and Engineering. The main research objective of the project is to uncover the atomic level structures and dynamics that govern the enhanced proton conductivity in compounds that can function as fuel cell electrolytes at intermediate temperatures (e.g. doped Sn-pyrophosphates and phosphate-solid-acid/silica composites). The main instruction objective is to build an x-ray facility (including both powder and single crystal instruments), where our students will acquire skills and experiences necessary to actively participate in a UTEP – National Laboratory research and instruction program.

1.2. Approach

There are three specific <u>research goals</u> related to the above-mentioned main research objective:

- 1) To identify the pathways and transport mechanisms that govern the enhanced proton conductivity in doped Sn-based pyrophosphates. The approach to achieve this goal will include:
 - Accurately determining the crystal structure and its temperature evolution for Sn_{0.9}In_{0.1}P₂O₇, the compound that has the highest proton conductivity among doped pyrophosphates. Modern x-ray powder diffraction techniques will allow atomic positions to be determined with sub-Ångstrom resolution.
 - Quantitatively determining salient features of the proton dynamics in the abovementioned compound, such as the probability of proton jumps between sites where protons (once incorporated) can temporarily reside, and the length of such jumps.

- Neutron vibrational spectroscopy and neutron quasielastic scattering will be used to accomplish this objective.
- Generating scenarios for the proton transport, and test them against the abovedescribed structural and dynamics information, as well as against previous knowledge from macroscopic-property measurements.
- 2) To reveal how certain doping-induced microscopic features (structural and dynamic) influence the efficiency of the proton conduction. The approach to achieve this goal will include:
 - Identifying subtle doping-induced structural features such as tetrahedral distortions, bond-length variations, etc. in the crystal structures of Sn_{1-x}M_xP₂O₇ (M=In, Sc, Al).
 - Determining, for each of the investigated doped pyrophosphate, proton-dynamics related quantities such as the proton jump probability and jump length.
 - Establishing connections, and possibly a pattern, between these doping-induced structural and dynamics features and the macroscopic proton conductivity.
- 3) To understand the effect of mixing solid acids CsH₂PO₄ and RbH₂PO₄ with dispersed silica (SiO₂) on the properties of their superprotonic phases. The approach to achieve this goal will include:
 - Determining the relationship between the composition and microstructure of the (1-x)CsH₂PO₄/xSiO₂ and (1-x)RbH₂PO₄/xSiO₂ composites and the proton conductivity of their high temperature phases.
 - Determining the thermal behavior of the solid-acid component upon heating under ambient and high-pressure, as a function of the silica content and average grain size.

There are also two specific <u>instruction goals</u> related to the above-mentioned main instruction objective:

1) To establish a core x-ray facility at UTEP, where both graduate and undergraduate students will receive hands-on training in scattering methods and techniques commonly used at national synchrotron x-ray and neutron facilities. The approach to achieve this goal will include:

- Securing internal matching funds from UTEP to purchase a single-crystal x-ray diffraction instrument (Bruker D8 Quest) that complements the one acquired from this DoD grant. Securing internal funds to renovate the x-ray facility room. Hiring a Ph.D. scientist to operate the facility and provide instruction to graduate/undergraduate students.
- Implementing protocols for facility operation and procedures for student instruction.
- 2) To involve students in sustainable research and instruction based on a UTEP National Laboratory Partnership Program. The approach to achieve this goal will include:
 - Initiate discussions with group leaders and managers at National Facilities, design and present plan for partnership aimed at student participation in experimental work carried out at National Laboratories
 - Secure external funding to implement the UTEP National Laboratory Partnership Program.

1.3. Relevance to the Army

Fuel cell technology offers unique advantages for both military and civil applications such as: low/zero emissions, few moving parts, portability, quietness, etc. The main potential applications for defense purposes (soldier power) are communications, sensors, battery chargers for caravans, special purpose vehicles (e.g. unmanned aerial and ground vehicles), and silent camp/watch capabilities. There are also multiple civil applications from appliances to the automotive industry. Many of the applications would tremendously benefit from fuel cell functionality at intermediate temperatures (between 150 and 300°C). Unfortunately, however, stable electrolytes that allow an efficient ion conduction within this temperature range are not as well developed or understood from the structural, physical and electrochemical perspectives as their low- and high-temperature counterparts. Our work is aimed at uncovering the microstructural and ion dynamics details that enable certain compounds to function as intermediate temperature fuel cell electrolytes. We believe that understanding and ultimately controlling these microscopic features will allow the rational design of high performance electrolytes through chemical manipulation.

2 SUMMARY OF THE MOST IMPORTANT RESULTS

2.1. Accomplishments for Reporting Period

Accomplishments related to research goals:

- Synthesized powders of In_xSn_{1-x}P₂O₇ of different doping levels 0<x<0.2, carried out temperature-resolved x-ray diffraction under different sample environments as a function of x, and performed LeBail and Rietveld refinements of the crystal structures
- Observed, for the first time, a salient structural feature (increase in the lattice parameter) that is specific for In_{0.1}Sn_{0.9}P₂O₇ (x=0.1 doping level), which is the sample that exhibits the highest proton conductivity
- Showed that the lattice parameter increase is not observed if the x-ray measurements
 are carried out on samples contained under vacuum; this is important because it can
 be corroborated with proton conductivity measurements carried out under vacuum to
 assess if the above-mentioned structural modification is related to the enhanced
 proton conductivity of In_{0.1}Sn_{0.9}P₂O₇
- Demonstrated the isomorphism between the superprotonic phases of CsH₂PO₄ and RbH₂PO₄ through structural refinements based on high-pressure, high-temperature xray diffraction data

Accomplishments related to instruction goals:

- Secured internal funds for the new UTEP research and student instruction x-ray facility
 to: acquire a new single-crystal Bruker D8 Quest diffractometer (\$270,000), hire a
 Ph.D. scientist/ postdoctoral to operate the facility and provide instruction to students
 (\$90,000 / 2 years), and renovate Rms. 134 and 132 in the Physical Sciences Building
 to house the facility (\$30,000)
- Established protocols for the use of the x-ray facility by other UTEP researchers and
 for student instruction; since the the facility became fully operational (Feb. 2015),
 more than 10 students of all levels from Ph.D. to undergraduate received
 instruction and actively participated in experiments, and 5 research groups from

- Physics, Chemistry, and Mechanical Engineering performed experimental work in the facility.
- Established contacts and collaborations with administrators and scientists at National Laboratories and wrote ~\$500,000 grant proposal to the Nuclear Regulatory
 Commission for joint research and student instruction projects between UTEP and Los Alamos National Laboratory.

2.2. Collaborations and Technology Transfer

- Synchrotron x-ray diffraction experiments on In_xSn_{1-x}P₂O7 carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure x-ray diffraction on CsH₂PO₄ and RbH₂PO₄ carried out at the National Synchrotron Light Source (Brookhaven National Laboratory)
- High-pressure neutron diffraction work on CsH₂PO₄ and RbH₂PO₄ carried out at the
 Manuel Lujan Neutron Scattering Center (Los Alamos National Laboratory)
- Neutron vibrational spectroscopy carried out on CsH₂PO₄ at the Manuel Lujan Neutron
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3. APPENDIXES

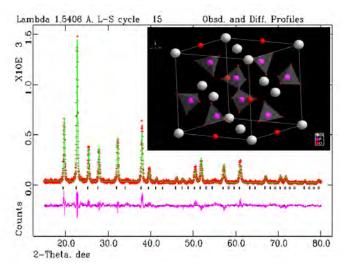
A. EXAMPLES OF RESEARCH PROJECTS

1) Cristian Botez – Physics

Crystal structures and proton conduction mechanisms in Sn_{1-x}In_xP₂O₇ pyrophosphates

The main goal of this research is to uncover the atomic-level structures and microdynamics responsible for the high proton conductivity of Indoped tin pyrophosphates. X-ray diffraction, enhanced by the use of modern in-house instrumentation and synchrotron radiation, is the first analytical technique we used in this project.

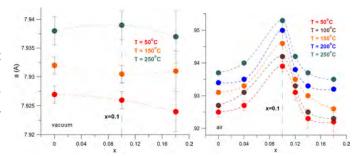
We have synthesized high-quality, impurity free samples of $Sn_{1-x}In_xP_2O_7$ (0<x<0.2), and used temperature-resolved x-ray diffraction data to structurally characterize them via LeBail (full profile) and Rietveld refinements (Figure 1).



Rietveld refinement of the crystal structure of $Sn_{0.9}In_{0.1}P_2O_7$ from x-ray diffraction data (red crosses). The green line is the calculated intensity, the lower trace is the difference between observed and calculated x-ray profiles, and the vertical bars are the Bragg reflection markers.

We first observed that the indium ion solubility limit of is \sim 0.12. We then found that the tetrahedral distortions (at different x values) are minimal, and consequently are not likely to play a key role in the proton conductivity enhancement observed for x=0.1. Instead,

analysis of the x dependence of the lattice constant of Sn_{1-x}ln_xP₂O₇, obtained from LeBail refinements of temperature-resolved x-ray data collected in air (Figure 2, left panel), demonstrate that the lattice



Lattice parameter dependence on the In doping level x in Sn_1 . $_xIn_xP_2O_7$ obtained from LeBail fits against x-ray diffraction data collected at different temperatures in air (left panel) and in vacuum (right panel)

constant exhibits a robust peak at x=0.1. This occurs at all temperatures used in our investigation, and suggests that the unit cell volume increase might facilitate the proton transport in this material. Interestingly, we found no lattice parameter increase at x=0.1 upon carrying out the same experiment

on $Sn_{1-x}In_xP_2O_7$ samples kept under vacuum during data collection (Figure 2, right panel). This observation is significant in view of recent proton conductivity results¹, and given the fact that these pyrophosphates do not nominally contain protons in the bulk. It also provides the first experimental evidence of a structural feature directly associated with the high proton conductivity of $Sn_{0.9}In_{0.1}P_2O_7$.

2) Luis Echegoyen - Chemistry

Perovskites as active layers in solar cells

Photovoltaics is a constantly changing and evolving field that involves the collection of light energy from the sun and its subsequent transformation into electrical energy. Specifically, our goal is to utilize a perovskite material (methylammonium lead iodide perovskite, CH₃NH₃Pbl₃) as the active layer of a solar cell. Recently, this has been the main focus of photovoltaic research with efficiencies starting at a mere 3.8% in 2009 and has already reached an astonishing 20.1% as of 2015 by the Korean Research

Institute of Chemical Technology (KRICT). ^{2,3} Shown in Figure 1 is our specific cell architecture involving CH₃NH₃PbI₃ as the light harvester. With this architecture we have been able to reach efficiencies of 11%, close to the reported efficiencies for similar architectures. The use of x-ray diffraction (XRD) is vitally important for the characterization of our perovskite layer, and data collected for our materials matches published results as shown in Figure 2 .⁴ We have future plans to use XRD as a primary method of characterization through varied angle and temperature studies of our samples.

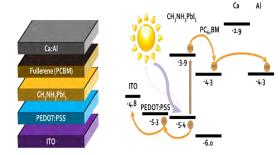


Figure 1 - Schematic representation of a working perovskite solar cell based on the PEDOT: PSS hole transport layer and PCBM electron transport layer.

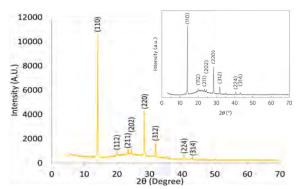


Figure 2 - XRD pattern recorded at the UTEP x-ray facility on the active CH₃NH₃PbI₃ layer of a solar cell (yellow line) compared to XRD pattern from Ref [3] (inset).

3) Yirong Lin - Mechanical Engineering

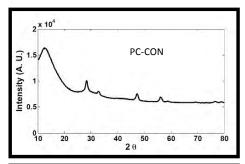
Synthesis of nanoparticles and nanowire hybrids

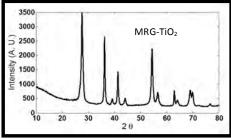
Synthesis of nano-hybrids is a complex process, where the proper crystallization of the active phase is paramount for the operation of these functional materials. From this point of view, x-ray diffraction (XRD) is a key technique that can accurately assess the quality of the synthesis of hybrid nano-systems. Below, we present two examples of such syntheses and corresponding XRD characterization

Porous Carbon/Cerium oxide nanoparticle (PC-CON) hybrids

The PC-CON hybrid synthesis is a one-step hydrothermal method. At first 100mg porous carbon (ACS Material, LLC) was dispersed in 200mL of deionized water (DI) water. Then 150mL of 0.02M Ammonium Cerium Nitrate (NH4)₂Ce(NO₃)₆ was added to the solution and the solution was sonicated for 45 minutes. The mixture was then separated by centrifugation. At this stage Ce(OH)₄ was formed on the pores and surfaces of the porous carbon. Then product was mixed with 100mL 5M NaOH solution and transferred into a Teflon lined autoclave. After heating the mixture for 45 hours at 180° C, the solution was separated by centrifugation, washed with DI water for three times. Then the remnant was dried at 70° C. At last the product was heated at 450° C in Argon for 2 hours.^{5,6}

The crystal structures of the PC-CON hybrid were determined utilizing a PANalytical Empyrean XRD using Cu K α radiation (Figure 1). The peak at ~13° represents porous carbon and rest of the XRD peaks indicate that the products were well crystallized and have a cubic fluorite structure of CeO $_2$ (space group: Fm3m) with lattice constant a=5.411Å, which is in agreement with the JCPDS file for CeO $_2$ (JCPDS 34-0394). No





X-ray diffraction patterns collected in the UTEP facility on hybrid samples of CeO_2 /porous carbon (upper panel), and TiO_2 /microwave reduced grapheme nanowires (lower panel). The data demonstrate that the desired active phases are presents in the nano-composites.

extra peaks corresponding to any other secondary phases were observed.

Microwave Reduced Graphene/Titanium dioxide nanowire (MRG-TiO₂) hybrids

The MRG-TiO₂ was synthesized following a simple hydrothermal method. 150mg microwave reduced graphene were transferred to a 250mL Pyrex glass bottle and mixed with a 50mL solution containing DI water and concentrated (37.3% Assay, Fischer Scientific) hydrochloric acid (HCl) with a 1:1 ratio. Subsequently, 2.5mL of the titanium tetrachloride (99.0% purity, Sigma Aldrich) was added dropwise to this solution. The glass bottle was then placed inside and aluminum cylinder and transferred into an oven at 160° C for 4 hours. After that, the resulting materials were rinsed several times with DI water and dried at 90° C for 30 minutes.

XRD data on the MRG-TiO₂ is shown in Figure 2. All the peaks matched with the standard diffraction data of TiO₂ (JCPDS, No. 76-1940). The XRD pattern exhibited strong diffraction peaks at 27°, 36° and 55° indicating that TiO_2 is in the rutile phase.⁷ No extra peaks corresponding to any other secondary phases were observed.

B. STUDENT INSTRUCTION / X-RAY SCATTERING FACILITY

The X-ray Scattering Facility at The University of Texas at El Paso is located in Rooms 134 and 132, Physical Science Building. The facility includes two powder and one single-crystal diffractometers:



Panoramic view of the new UTEP x-ray scattering facility

- A new PANalytical Empyrean powder x-ray scattering system equipped with an Anton Paar XRK 900 solid-gas reaction chamber and an ultrafast PIXcell^{3D} detector (sponsored by this DoD grant). The system has unique characteristics. The XRK 900 is the only chamber on the market that allows reactive gas flow through a polycrystalline sample (at different temperatures, pressures and flow rates), enabling it to replicate conditions under which functional materials actually operate. Structural and/or chemical modifications induced by variable sample environments that occur on time scales from a few seconds to tens of hours can be tracked in real time by the PIXcel^{3D} detector. The system includes state-of-the-art software that allows chemical change/phase transition identification and ultra-precise (+/- 0.01Å) quantitative determinations of lattice parameters, atomic positions, and bond lengths.
- A Siemens D5000 powder x-ray diffractometer equipped with an MBraun position sensitive detector for rapid data collection and a Paar TTK chamber for temperature control. The instrument allows Rietveld-refinement-quality powder diffraction patterns corresponding to a 20°-60° 20 range (χ =1.5406Å) collected in the reflectivity geometry in about 90 min. at temperatures between 25 and 500°C. Within this range the temperature is stable to 0.1°C.
- A new Bruker D8 single-crystal diffractometer equipped with a Photon 100 large area detector and low temperature (80 K) capabilities (sponsored by UTEP). The system allows rapid data collection for crystal structure determination. Powder samples can also be run in the in the transmission (capillary mode) mode

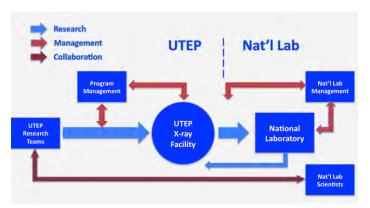


Students working on the Panalytical Empyrean and Bruker D8 Advance diffraction systems in the new X-ray Scattering Facility at The University of Texas at El Paso

Student instruction in modern x-ray scattering techniques and student participation in research projects relevant to the DoD mission is a priority within our x-ray scattering facility. Since the facility became fully operational in February 2015, more the 10 undergraduate and graduate students have

received such instruction, became able to operate the instruments independently, and actively participated in research. Collaborations with other groups at UTEP are also important; we have developed protocols for facility access by researchers within the Colleges of Science and Engineering, and so far 5 such groups have used our instrumentation and collected x-ray data important for their research projects.

Our next goal is to use the x-ray facility as a key component of a UTEP — National Laboratory Partnership Program that, we believe, will afford unique, career-defining opportunities to our minority students. We will engage our faculty and students in multidisciplinary research projects that are initiated and carried out primarily at UTEP but have a well-defined component to be performed at a partner synchrotron and neutron laboratory. We have already established contacts and collaborations with



Flowchart of the UTEP – National Laboratory Partnership Program operation

administrators and scientists at National Laboratories and wrote a grant proposal to the Nuclear Regulatory Commission to fund the program's implementation.

Our program will function as follows:

- Multidisciplinary teams of faculty and students from the Colleges of Science and Engineering will design projects aimed at investigating functional materials and propose experiments that are initiated in our newly developed x-ray facility, but have a component that requires the use of synchrotron x-rays and/or neutrons.
- UTEP program management will assess the feasibility and prospects for success of the proposed work, and selected teams will receive theoretical and hands-on instruction before starting their work.
- Teams will carry out experiments in the UTEP x-ray facility aimed at confirming the quality of their samples, collecting preliminary data, and familiarizing themselves with techniques and experimental setups they will encounter at National Laboratories.
- Teams will travel to national synchrotron and neutron laboratories, perform experiments, and interact with members of the "user" community and National Laboratory scientists, setting the basis for long term collaborations and joint grant proposals.
- Teams will return to UTEP, continue working on their projects in the UTEP x-ray facility, and prepare for the next set of experiments at the National Laboratories

The program, whose proper implementation and sustainability critically depends on the UTEP x-ray facility, would tremendously benefit our minority and underprivileged students. They will do research at some of the best facilities in the world, and demonstrate that once offered the same sustained level of instruction and access, they can perform as well as any of their peers.

4. BIBLIOGRAPHY

- 1. Nagao et al., J. of Electrochem. Soc. **153** (8), A1604 (2006).
- 2. A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, J. Am. Chem. Soc., **2009**, 131, 6050.
- 3. Best Research-Cell Efficiencies. Digital image. National Center for Photovoltaics. National Renewable Energy Lab, 5 Feb. **2015**.
- 4. N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, and S. Seok, Nat. Mater., **2014**, 13, 897
- 5. Padmanathan, N., and S. Selladurai. "Shape controlled synthesis of CeO2 nanostructures for high performance supercapacitor electrodes." RSC Adv.4.13 (**2014**): 6527-6534.
- 6. Li, Changqing, et al. "Controllable preparation and properties of composite materials based on ceria nanoparticles and carbon nanotubes." Journal of Solid State Chemistry 181.10 (2008): 2620-2625.
- 7. Hu, Wanbiao, et al. "Tailoring the nanoscale boundary cavities in rutile TiO 2 hierarchical microspheres or giant dielectric performance." Journal of Materials Chemistry 20.39 (2010): 8659-8667.